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Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using Date Palm Leaves.

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Abstract

The ability of Date palm Leaves powder (DPLP) to remove methylene blue (MB) from aqueous solutions by the biosorption process has been studied. Biosorption studies were carried out at different initial dye concentration, contact time, initial solution pH, biosorbent dosage, the particle size of (DPLP) and temperature. Biosorption data were modeled using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms. The results showed that equilibrium was reached within 160 min. The used biosorbent gave the highest adsorption capacity at pH 6.5 . Equilibrium data of the biosorption process fitted very well to the Temkin model (R^2=0.994). The maximum adsorption capacity, Langmuir's qmax, improved from 43.103 to 58.14 mg/g as the temperature increased from 30 to 60°C. The enthalpy ΔH° and entropy ΔS° values were respectively estimated at 8.098 kJ mol^{-1} and 12.97 J K^{-1} mol^{-1} for the process. Three simplified kinetic models including a pseudo-first-order equation, pseudo-second-order equation and intraparticle diffusion equation were selected to follow the adsorption process. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was shown that the adsorption of methylene blue (MB) could be described by the pseudo-second order equation (R^2= 0.996), methylene blue is slowly transported via intraparticle diffusion into the particles and is finally retained in micropores, suggesting that the adsorption process is presumable a physisorption.

Keywords: Date palm leaves, Adsorption, methylene blue, Isotherm, Kinetics, Thermodynamics;

1. Introduction

It is reported that there are over 100,000 commercially available dyes with a production of over 7×105 metric tonnes per year [1]. Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents [2]. The released dye in water streams represents a risk of ecotoxicity and a potential danger of bioaccumulation [3]. Methylene blue is not regarded as acutely toxic, but it can have various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing,

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while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. A large amount creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturition, and methemoglobinemia-like syndromes [4]. Therefore, removal of Methylene blue from wastewater is most desirable. A range of conventional treatment technologies for dye removal have been investigated extensively, such as biological treatment, adsorption, chemical oxidation, coagulation, and reverse osmosis [5]. Adsorption was found to be superior to other techniques for water re-use in terms of simplicity of design, ease of operation and insensitivity to toxic substances [6]. Although Granular activated carbon has been designated by the Environmental Protection Agency of USA as the best available technology for organic chemicals removal, it is still considered expensive adsorbent and the higher the quality the greater the cost. Both chemical and thermal regeneration of spent carbon is expensive, impractical on a large-scale and produces additional effluent and results in considerable loss of the adsorbent. This has led many workers to search for the use of cheap and efficient alternative materials [7]. These include spent corncob substrate [8]; pomelo (Citrus grandis) peel [9]; Luffa cylindrica fibers [10]; sunflower seed shells [11]; olive pomace [12]; Posidonia oceanica (L.) fibres [13]; wheat shells [14]; palm kernel fibre [15] and phoenix tree's leaves [16] .

Date palm (Phoenix dactylifera L.) is a member of the family Arecaceae (palm family). In this work, we attempt to use Date Palm leaves, an agricultural waste abundantly available in the south of Algeria as a sorbent to remove methylene blue from aqueous solution.

2. Materials and Methods

2.1. Materials

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature and Methylene blue concentration. The experiments were carried out in 250 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 mL. The equilibrium concentrations of the solution samples were analyzed using UV-Vis spectrophotometer (Model SHIMADZU 1800) Standard calibration curve was prepared by recording the absorbance values of various concentration of methylene blue dye at maximum absorbance of wavelength (668 nm). The surface of date palm leaves fibers were observed with a Hitachi S4700 field emission scanning electron microscope after coating them with 4nm of platinum/palladium in a Agar model 208HR high resolution sputter coater. A HANNA instrument pH meter was used for pH measurements, A magnetic stirrer was used to agitating the samples.

2.2. Biosorbent

The Date palm leaves were collected from Ouargla (Algeria) region palm trees, the collected materials were washed with distilled water for several times to remove all the dirt particles and laid flat on clean table to dry. Dry leaves were grounded with grinder. After, the leaves particles were sieved by using available sieves of nominal sizes (74, 149, and 250 μm). This produced a uniform material for the complete set of adsorption tests, which was stored in an air-tight plastic container for all investigations. Particle sizes of 74μm were used in all experiments throughout this work; the other sizes 149 and 250 μm were used only for particle size effect study. The main components of the date palm leaves are cellulose 38.10% , hemicellulose 22.74%, lignin 11.95%, ash 7.71%.

2.3. Biosorbate

Methylene blue used in this study was of commercial purity (FW, 319.86; MF, $C_{16}H_{18}N_3SCl$). Stock solution of methylene blue (1000 mg L^{-1}) was prepared by dissolving the required quantity of the dye in double-distilled water. Experimental dye solution was prepared by diluting the stock solution with suitable volume of double-distilled water to the desired concentration. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or HCl.

2.4. Biosorption studies

The adsorption experiments were carried out by batch process, 1.00 g of biosorbent was placed in Erlenmeyer flasks with 100 mL solution of methylene blue of desired concentration. The mixture was agitated at 100 rpm at 30, 45 and 60°C. The contact time was varied from 0 to 220 minutes. At predetermined time, the flasks were withdrawn from the agitator and the reaction mixtures were filtered through Whatman filter paper No. 40. For thermodynamic study, the experiment was performed using 1g DPL powder added to 100 mL of methylene blue solution in 250 mL flasks. The agitation was at 100 rpm for 160 min at pH=6.5 . All the experiments were performed in duplicates. The amount of methylene blue adsorbed at equilibrium per unit mass of biosorbent was determined according to the following equation:

$$qe = \frac{(C_0 - Ce) * V}{m} \qquad (1)$$

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of methylene blue (mg/L), Ce is the equilibrium concentration of the adsorbate (mg/L) in solution and qe is the methylene blue quantity adsorbed at equilibrium (mg/g). For the calculation of methylene blue rate adsorption (R %), the following expression was used:

$$R(\%) = \frac{(C_0 - Ce) * 100}{C_0} \qquad (2)$$

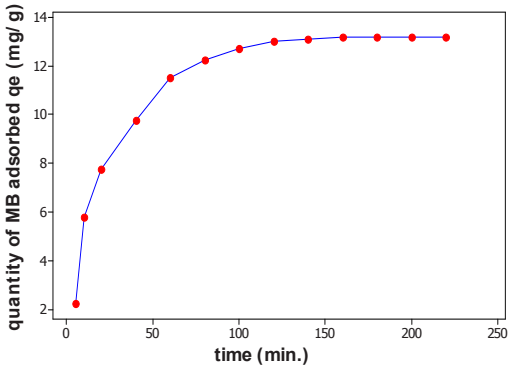

Fig. 1. Effect of equiliberium time for MB on DPLP. Conditions : pH 6.5, adsorbent dosage 1.00g/100ml, particle size 74µm, and temperature 30°C

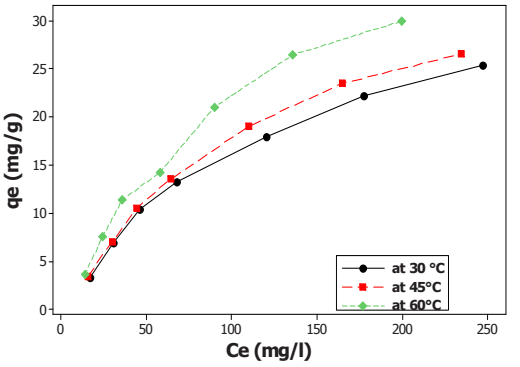

Fig. 2. Adsorption isotherms of MB on DPLP at different T°C

2.5. Effect of contact time

Results depicted in Fig. 1 clearly show that the adsorption of methylene blue onto DPLP reached equilibrium in 160 min. Adsorption first followed linear rising in which instantaneous, extremely fast uptake takes place, and then a stationary state was observed. The fast initial uptake was due to accumulation of methylene blue on surfaces of DPLP adsorbents which is a rapid step. It was concluded that 160 min was sufficient for adsorption to attain equilibrium.

2.6. Effect of particules size

The effect of particle size on removal of methylene blue was studied with different sizes from 74 to 250 μm. The removal efficiency of methylene blue by DPLP increases from 35.8 to 66.1 % as the particle size decreases from 250 to 74μm for an initial concentration of 200 mg/l . The extent of the adsorption process increases with increased specific surface area. The specific surface available for adsorption will be greater for smaller particles, and hence adsorption efficiency of methylene blue increases as particle size decreases. For larger particles, the diffusion resistance to mass transport is higher, and most of the internal surface of the particle may not be utilized for adsorption. Consequently, the amount of MB adsorbed is small.

2.7. Effect of solution pH

The effect of pH on the amount of MB adsorbed onto DPLP was investigated over the pH range from 2 to 8. The pH was adjusted using 0.1 mol l^{-1} NaOH or 0.1 mol l^{-1} HCl solutions. In this study, 100ml of MB solution of 200 mg l^{-1} was agitated with 1 g l^{-1} of DPLP. Agitation was made for 160 min and the adsorption mixture was filtered to separate the DPLP from the solution. It found that the higher adsorbed amount of MB was at pH 6.5 .

2.8. Adsorption isotherms

The four most common adsorption isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), were applied to understand the adsorbate–adsorbent interaction. The Langmuir equation can be described by the linearized form [17].

$$\frac{Ce}{qe} = \frac{1}{K_L * q_{\max}} + \frac{Ce}{q_{\max}} \qquad (3)$$

where qe is the adsorption capacity at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g), K_L is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption, and Ce is the equilibrium solution concentration (mg/l). According to Bouhamed et al. [17] the essential features of the Langmuir isotherm can be expressed in terms of separation factor or equilibrium parameter R_L that can be calculated from the relationship :

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where C_0 is the highest initial concentration (mg/l). The value of R_L indicates whether the type of isotherm is irreversible adsorption (R_L=0), favorable adsorption 0< R_L < 1 unfavorable adsorption (R_L>1), or linear adsorption (R_L=1). In this study, R_L for DPLP had values less than 1, indicating favorable adsorption. The linearized Freundlich isotherm equation is represented by the following equation [17]:

$$Log(qe) = Log(K_F) + \frac{1}{n} Log(Ce) \quad (5)$$

Where K_F is the Freundlich constant (mg/g) and 1/n is the adsorption intensity. Log(qe) was plotted against log(Ce) and a straight line was fitted in the data. The D-R equation is given by Dubinin et al. [17]:

$$Ln(qe) = Ln(q_m) - \beta\varepsilon^2 \quad (6)$$

where qe is the amount adsorbed onto adsorbent at equilibrium (mg/g), qm is the D-R monolayer capacity (mg/g), β is a constant related to sorption energy (mol^2kJ^{-2}), and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RTLn\left[1 + \frac{1}{Ce}\right] \quad (7)$$

where R is the gas constant (8.3145 J $K^{-1}mol^{-1}$), T is the temperature in K. The mean energy of adsorption (E) is calculated by using the following formula [17]:

$$E = (2\beta)^{-0.5} \quad (8)$$

The Temkin isotherm also used in this study to fit with the experimental data, and it can be represented as:

$$qe = BLn(Ce) + B\ln A \quad (9)$$

where A and B are Temkin isotherm constants. Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate

interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. All of the constants are presented in Table 1.

Table 1. The Values of Parameters for Each Isotherm Model Used in The Studies.

		Langmiur isotherm constants			Freundlich isotherm constants		
T°C	qmax (mg/g)	K_L	R_L	R^2 (%)	K_F	n	R^2 (%)
30	43,103	0,006	0,455	95,1	0,541	1,379	95,4
45	47,619	0,0058	0,463	96,0	0,535	1,341	96,6
60	58,14	0,0058	0,463	91,2	2,032	1,761	88,8
		Temkin isotherm constants			D-R isotherm constants		
T°C		A	B	R^2 (%)	$q_{m,D-R}$	E (KJ/mol)	R^2 (%)
30		0,0787	8,3	99,4	17,81	0,0749	85,5
45		0,0796	8,89	99,0	18,17	0,0846	82,3
60		0,0879	10,2	98,2	18,73	0,099	85,0

2.9. Thermodynamic parameters

The mechanism of adsorption may be determined through thermodynamic quantities such as change in Gibbs free energy (ΔG°), change in enthalpy of adsorption (ΔH°), and change in entropy (ΔS°). The thermodynamic equilibrium constant K_d can be calculated using Eq. (10):

$$K_d = \frac{C_{ad}}{C_e} \quad (10)$$

The increase in Kd with increase in temperature indicates the endothermic nature of the process. The ΔG°, ΔH°, and ΔS° were calculated using the equations:

$$\Delta G° = -RTLn(K_d) \quad (11)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (12)$$

A plot of Ln(Kd) versus 1/T was found to be linear, ΔH° and ΔS° were determined from the slope and intercept of the plot, respectively.

Table 2. Thermodynamic parameters calculated for the adsorption of MB on DPLP

T°C	K_d	ΔG°(Kj/mol)	ΔH° (Kj/mol)	ΔS°(j/mol.K)	R^2 (%)
30	0,194118	4,1298			
45	0,216456	4,0463	8,0983	12,9706	97,1
60	0,259712	3,7327			

2.10. Kinetic studies

A quantitative understanding of the sorption is possible with the help of kinetic models. The pseudo-first-order kinetic model [17], can be written as:

$$Log(qe - q_t) = Log(qe) - K_1.t / 2.303 \qquad (13)$$

where qe and q_t are the amounts of MB (mg/g) at equilibrium and at time t, respectively, and K_1 is the pseudo-first-order equilibrium rate constant (1/min). A plot of log(qe - qt) vs t gives straight line confirming the possibility of the applicability of the pseudo-first-order rate equation (R^2 = 95.80 %). Pseudo-second-order sorption rate equation may be expressed as follows [17]:

$$\frac{t}{q_t} = \frac{1}{K_2 qe^2} + \frac{1}{qe}.t \qquad (14)$$

Where h = K_2qe^2 (mg/g.min) can be regarded as the initial adsorption rate as t→0 and K_2 (g/mg.min) is the rate constant of pseudo-second-order adsorption . The plot t/qt versus t should give a straight line if pseudo-second-order kinetics is applicable and the qe, K_2 and h can be determined from the slope and intercept of the straight lines in plot of t/qt versus t. Because Eqs. (13) and (14) can not identify the diffusion mechanisms, the intraparticle diffusion model was considered in order to determine the participation of this process in the sorption of methylene blue by DPLP. In this model, the rate of intra-particle diffusion is a function of $t^{1/2}$ and can be defined by Eq. (15) as follows [17]:

$$q_t = K_P t^{1/2} \qquad (15)$$

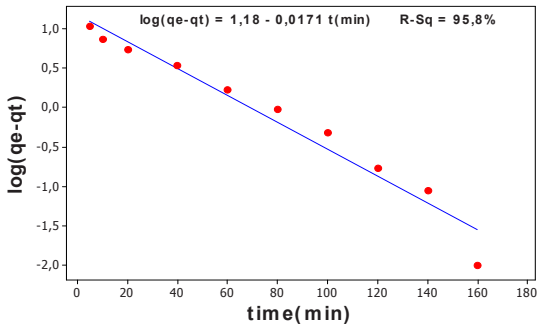

Fig. 3. The Pseudo-First-Order kinetic of MB adsorption on DPLP at 30°C

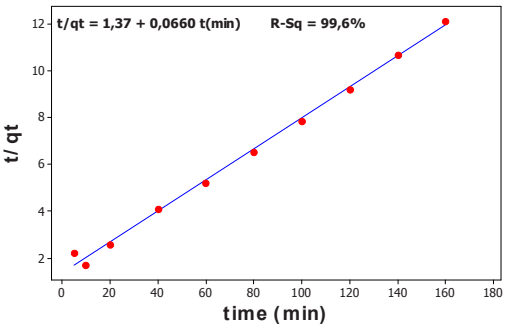

Fig. 4. The Pseudo-Second-Order kinetic of MB cadsorption on DPLP at 30°C

where K_p is the intraparticle diffusion rate constant, (mg/g.$min^{1/2}$). Such plots may present a multilinearity[18], indicating that two or more steps take place. The first, sharper portion is the external

surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. Fig. 5. shows a plot of the linearized form of the intraparticle diffusion model at concentrations studied. As shown in Fig. 5., the external surface adsorption is presened in stage 1. which is completed before 10 minutes, and then the stage of intraparticle diffusion control (stage 2) is attained and continues from 10 to 60 minutes. Finally, equilibrium adsorption (stage 3) starts after 60 minutes. The methylene blue is slowly transported via intraparticle diffusion into the particles and is finally retained in the micropores. In general, the slope of the line in stage 2 is called as intraparticle diffusion rate constant[18].

Table 3. Comparison between the Adsorption Rate Constants, qe Estimated and Correlation Coefficients Associated with Pseudo-first-order and the Pseudo-second-order Equation and Intraparticle Diffusion

Pseudo-first-order Constants			Pseudo-second-order Constants			
K_1 (min^{-1})	qe(mg/g)	R^2 (%)	K_2 (g/mg.min)	qe(mg/g)	h(mg/g.min)	R^2 (%)
0,00743	15,136	95,8	0,0032	15,152	0,7299	99,6

Intraparticle diffusion constant	
Kp(g/mg,$min^{1/2}$)	R^2 (%)
1,23	99,6

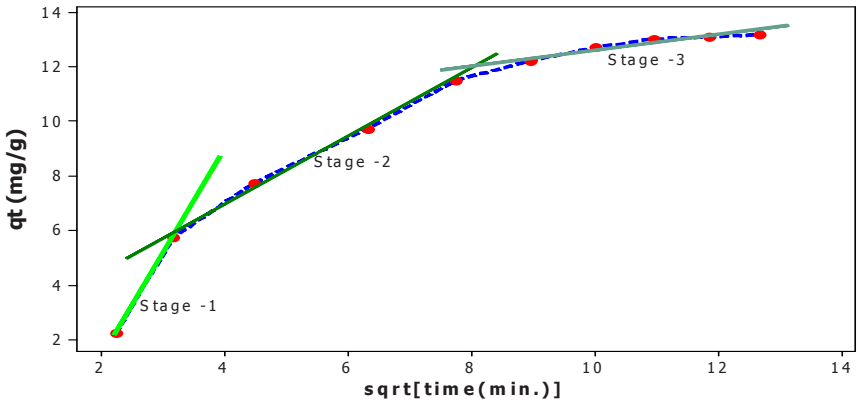

Fig. 5. Intraparticle Diffusion plot for MB Adsorbed onto DPL Powder at C_0= 200mg/l ; pH =6.5 particle size 74 µm, and T= 30°C

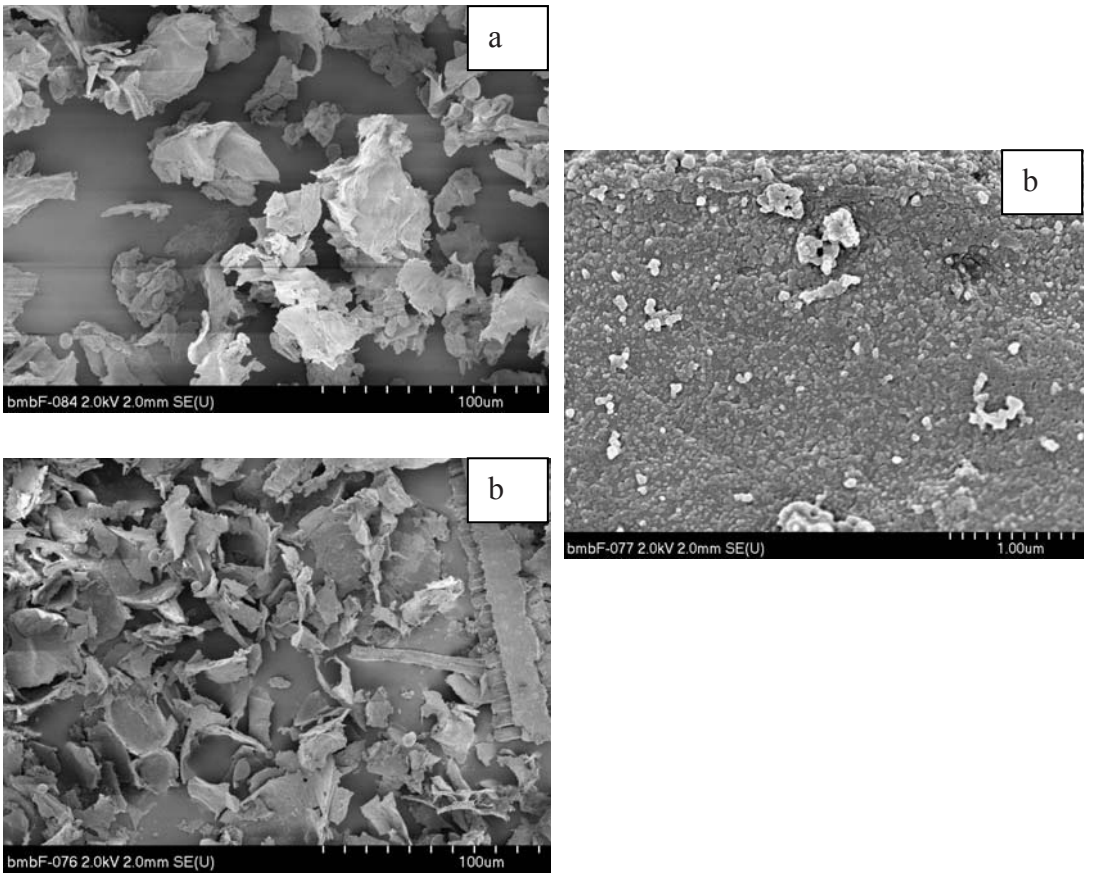

Fig. 6. SEM images of DPLP (a) before adsorption of MB (b) after adsorption of MB

3. Conclusion

Equilibrium, kinetic and thermodynamic studies were made for the adsorption of MB from aqueous solution onto DPL powder at pH 6.5 . The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Temkin isotherm was demonstrated to provide the best correlation for the sorption of MB onto DPL powder. The adsorption of MB can be described by the intraparticle diffusion model up to 60 min. The intraparticle diffusion model indicates that the external surface adsorption (stage 1) is completed before 10 min, and final equilibrium adsorption (stage 3) is started after 60 min. The MB is slowly transported via intraparticle diffusion into the particles and is finally retained in micropores. The pseudo second-order kinetic model agrees very well with the dynamical behavior for the adsorption of MB onto DPL powder. It may be concluded that DPL powder may be used as a low-cost, natural and abundant source for the removal of MB from the wastewater.

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